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A thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
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# ELECTROWINNING VERSUS ELECTROREFINING OF BLISTER COPPER

## I. PURPOSE OF INVESTIGATION

The loss of interest on the value of the copper tied up as anodes in the electrorefining process is one of the major complaints of this method of copper production. Assuming an electrorefining plant with a monthly production of 18,000,000 pounds of copper, I have calculated that, at an interest rate of 5 per cent, this plant would lose $108,000 in interest per year due to anode tie-up. This calculation was made on the basis that, at any time during the process, half (9,000,000 pounds) of the monthly production is tied up in the form of anodes, and that the interest on the value of this amount of copper is lost. I used 24 cents per pound to calculate the value of the copper.

In addition to the $108,000 lost on anode tie-up, the anode scrap which must be remelted and recast amounts to about 2,000,000 pounds per month. Calculated on the same basis as previously stated, this scrap is responsible for a loss in interest of about $24,000 per year. Thus, a loss of $132,000 per year is realized in an electrorefining plant with a capacity of 18,000,000 pounds of copper per month.

The purpose of my investigations is to determine whether or not some method of electrowinning could, on the basis of the $132,000 interest loss, economically replace the electrorefining method of copper production. Specifically, my

thesis is concerned with the roasting of molten blister copper, the leaching with a sulfuric acid solution of the cuprous oxide formed, and the electrowinning of the copper from the leach solution. In the following sections of this report, I will discuss as fully as possible both the theoretical and practical aspects of the roasting, leaching, and electrowinning steps, as well as the economic considerations of the process. The results of my laboratory work will, of course, be integrated to the process.

## II. LABORATORY PROCEDURE AND THEORY

Throughout the course of my laboratory work, I strived to approximate as closely as possible actual plant conditions. In some instances, however, it was impossible to duplicate plant operations because of the limits of laboratory equipment. In any case, I will attempt to correlate laboratory procedure and theory with conditions that can be realized on an operating plant scale.

### A. Roasting of Blister Copper

The roasting of molten blister copper by an air blow across the molten bath is a faster and cheaper method of oxidizing copper than any other possible method. This method of roasting will be developed from a practical viewpoint, but is not feasible on a laboratory scale. Therefore, the laboratory roasting was done by heating thinly-spread, granular blister copper in fireclay dishes. Large gas burners supplied the necessary heat and natural draft furnished an ample supply of fresh air. At 30 minute intervals I sprayed a small stream of water on the hot copper in order to break off the thin scale of CuO and thus present a fresh surface for further oxidation. The spray was introduced through small openings in wire screens which were placed over the fireclay dishes to prevent the loss of the CuO scale.

At the temperatures achieved in the laboratory roast (400-500°C), a thin film of CuO will form on the exterior of

the copper particle in a comparatively short time. Under the thin CuO film is a relatively thick inner layer of $Cu_2O$. After a very thin layer of oxide is formed, subsequent oxidation occurs directly as the square root of the roasting time. [1:622-623] CuO is soluble in a dilute sulfuric acid solution according to the equation $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$. Likewise, $Cu_2O$ is soluble in a sulfuric acid solution according to the equation $Cu_2O + H_2SO_4 \rightarrow CuSO_4 + H_2O + Cu$, indicating that a certain amount of metallic copper will be liberated during leaching which must be returned to the roasting step. This condition resembles actual plant roasting because only $Cu_2O$ is formed at the temperature at which plant roasting would be done.

Blister copper usually is 98 per cent or more pure copper and the remainder contains such impurities as iron, antimony, bismuth, zinc, nickel, lead, sulfur if the blister is underblown, and oxygen, if overblown. [2:178] These impurities will be oxidized along with copper, and their oxides, if soluble in a sulfuric acid solution, will be present in the electrolyte. However, antimony, bismuth, and sulfur form volatile oxides so these elements probably will not appear in the electrolyte. If the blister to be roasted is overblown in the converter, the amount of $Cu_2O$ thus formed should reduce the amount of blowing required in the roasting furnace.

B. Leaching the Oxide

Every three hours, I removed the roasted material from

the roasting dishes and dissolved the oxide in a 6 per cent sulfuric acid solution (110 grams per liter). With frequent stirring, a one-half hour leach was sufficient to cause dissolution of all the CuO and $Cu_2O$ present. Following leaching, I filtered the solution off and dried the remaining copper which was returned to the roasting step. In order to obtain a solution of known copper concentration, I weighed the granular blister copper before roasting and again after leaching.

Since iron and nickel oxide are not appreciably attacked by sulfuric acid, probably the only impurity in solution will be a minute quantity of zinc. A solution of such purity is not often realized in a practical hydrometallurgical process.

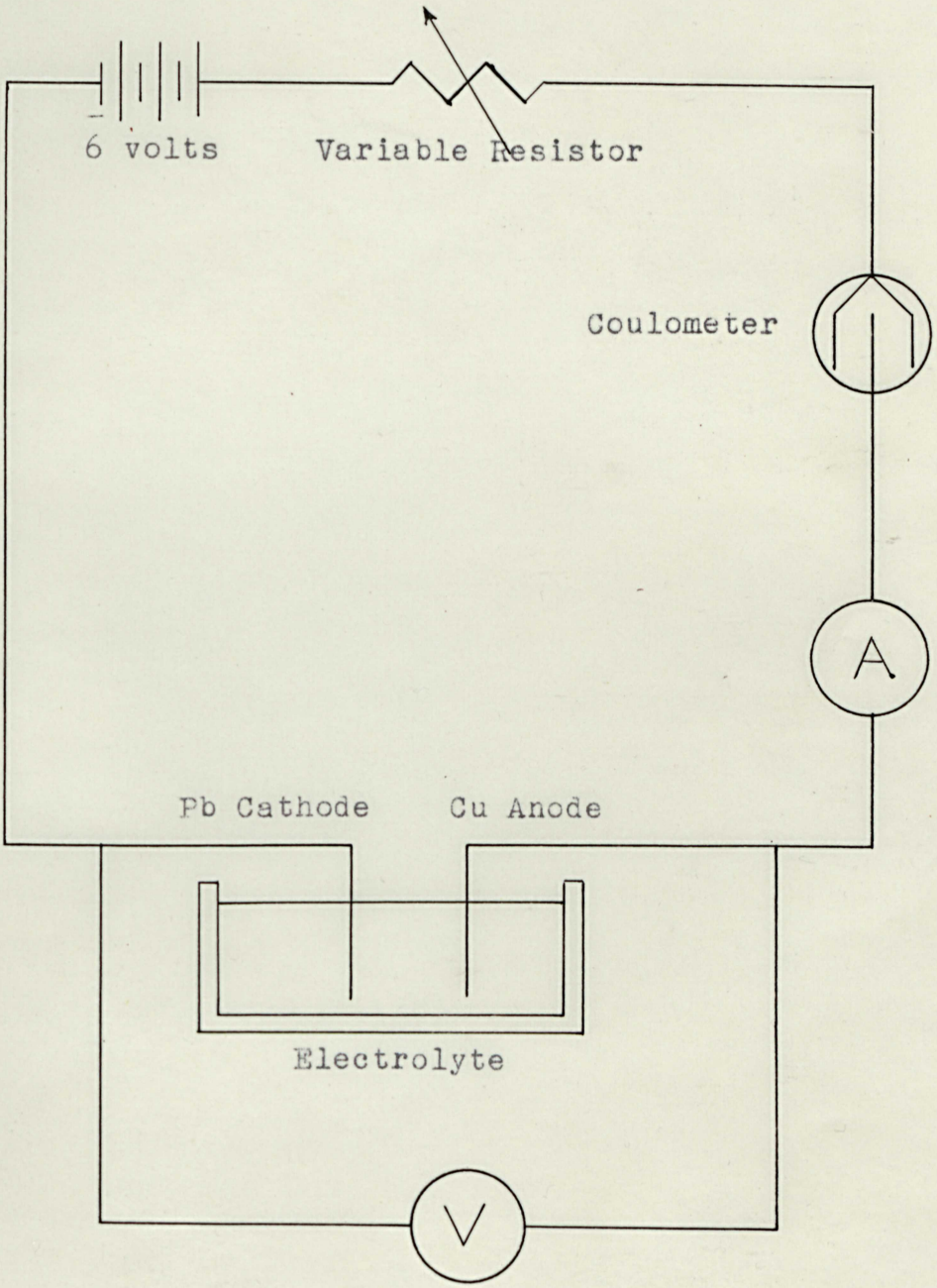
C. Electrowinning

This phase of my laboratory work approximates more closely actual conditions than either roasting or leaching. Consequently, I will be able to better correlate experimented results to practical considerations.

Figure 1 shows the diagramatic arrangement of my electrowinning equipment. A 6-volt rectifier supplied the power; a 170-ohm variable resistor regulated current flow; and a standard copper coulometer measured the quantity of current. A laboratory ammeter was used to give an approximate indication of current flow and a voltmeter across the cell measured cell voltage. Stirring of the copper solution was accomplished with a variable-speed electric stirrer. The

Figure 1

Schematic of Laboratory Electrolysis



solution was contained in a 2-liter rectangular glass tank. The cathode starting sheet was made of rolled copper sheet and the anode was cast lead.

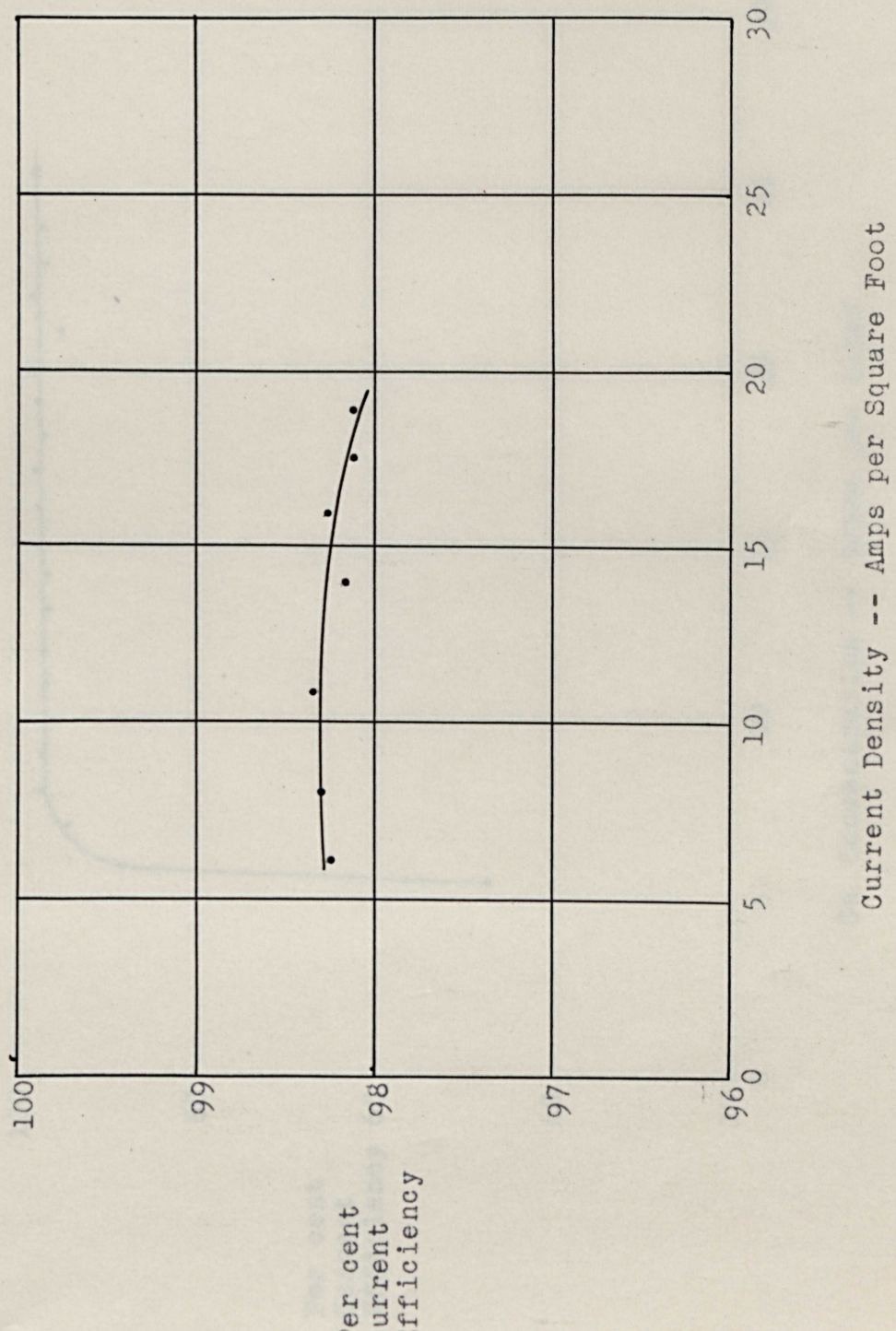
As previously explained, the purity of the leach solution should be high. Therefore, with an almost pure copper sulfate solution, current efficiency should be higher than that usually attained in the general run of electrowinning operations.

In order to determine current efficiencies at various current densities, I prepared for electrolysis a solution containing 20 grams of Cu and 70 grams of free acid per liter. These values were chosen as the mean values of concentrations ordinarily used in electrowinning practices. [3] The results of this procedure are shown on Graph 1. It is seen that efficiencies of over 98 per cent can be obtained between current density values of 6 to 17.6 amperes per square foot. Above 18 amperes per square foot, laboratory results indicated a downward trend in current efficiency, but the accuracy of this indication is doubtful since the coulometer cathode showed evidences of burning at this point. However, very good efficiencies can be obtained over the range indicated on Graph 1.

Having established that efficiency is high over a considerable range of current densities, I next determined the effect of concentration on current efficiency. I started with a solution containing 26 grams of copper and 70 grams of acid per liter and used a current density of 9.0 amps per square foot, a value within generally applied limits of current

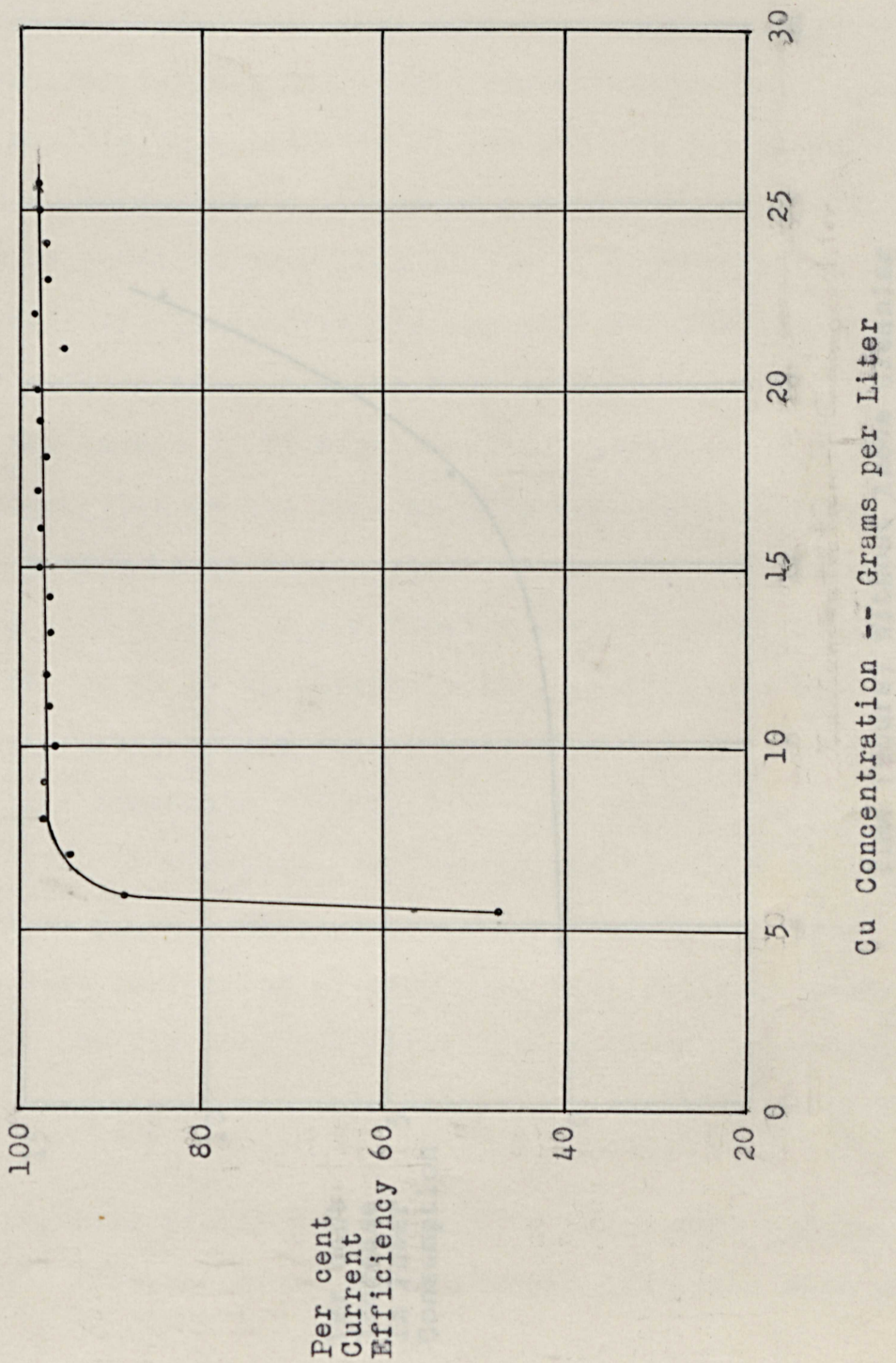
Graph 1

Current Efficiency Versus Current Density



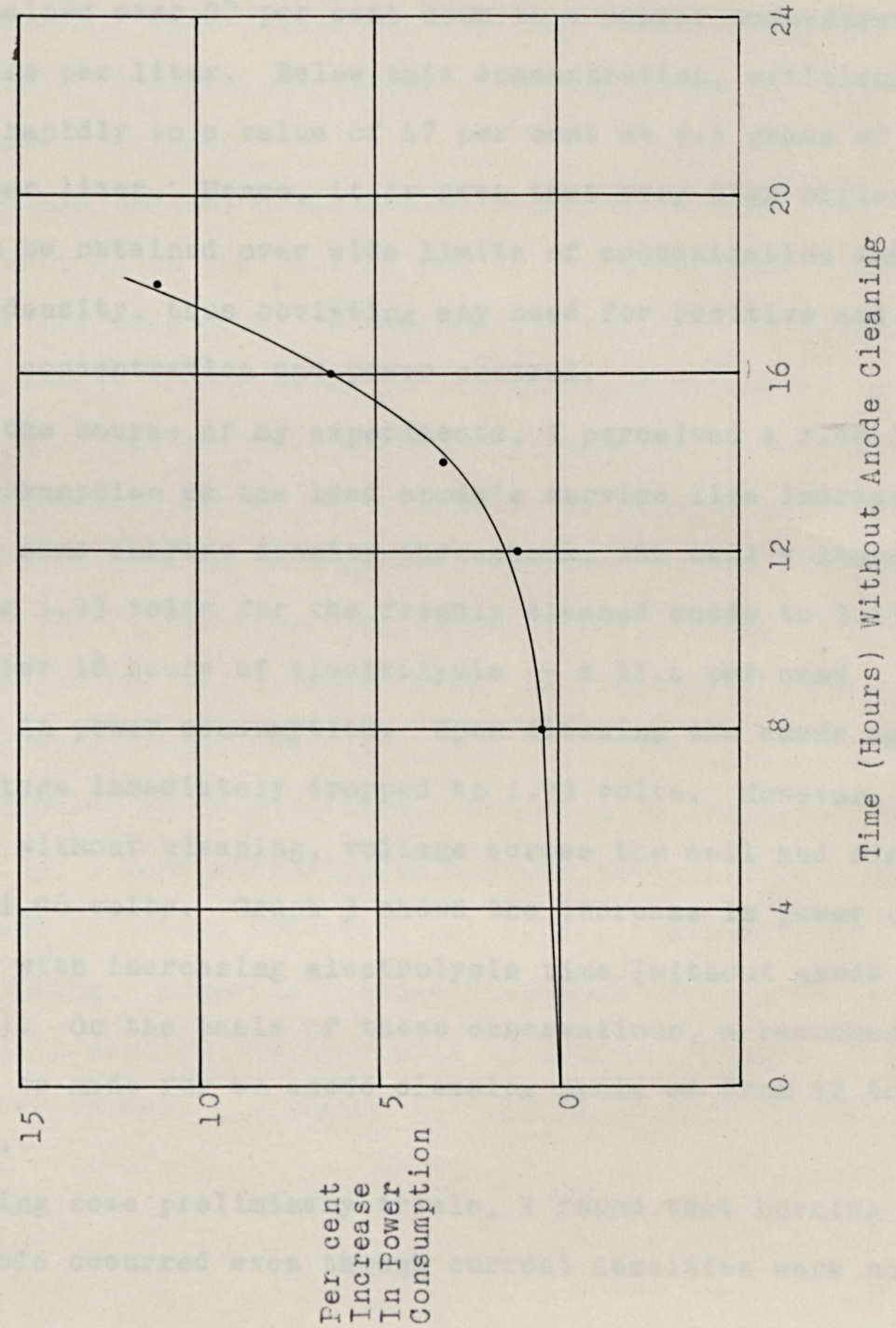
Graph 2

Current Efficiency Versus Copper Concentration



Graph 3

Variation in Power Consumption With Anode Age



density in practical operations. [2:331] The solution was stripped in steps of approximately 1 gram of copper per liter and efficiencies calculated. Graph 2 shows the results of this procedure. As shown by the graph, current efficiencies remained over 97 per cent down to a copper concentration of 8 grams per liter. Below this concentration, efficiency dropped rapidly to a value of 47 per cent at 5.5 grams of copper per liter. Hence, it is seen that very high efficiencies can be obtained over wide limits of concentration and current density, thus obviating any need for positive and definite concentration and power control.

In the course of my experiments, I perceived a rise in power consumption as the lead anode's service life increased. With the same current density throughout, the cell voltage rose from 1.93 volts for the freshly cleaned anode to 2.15 volts after 18 hours of electrolysis -- a 11.4 per cent increase in power consumption. Upon cleaning the anode again, cell voltage immediately dropped to 1.93 volts. However, at 12 hours without cleaning, voltage across the cell had risen to only 1.96 volts. Graph 3 shows the increase in power consumption with increasing electrolysis time (without anode cleaning). On the basis of these observations, a recommendation can be made for an anode cleaning cycle of from 12 to 14 hours.

During some preliminary trials, I found that burning of the cathode occurred even though current densities were not

exceptionally high. This phenomenon was due to an improverishment in copper ions of the solution immediately surrounding the cathode. To reduce this effect, I set up a stirrer which served to keep the concentration of the solution more uniform at all points. This innovation enabled the precipitation of an adherent, fine-grained copper layer and caused an increase in current efficiency.

Although current efficiencies attained in this problem are higher than in the general run of electrowinning operations, 8 to 10 times more power is customarily required to deposit the same amount of copper as in the multiple system of refining. [3]. The multiple system will produce between 165 and 180 pounds of copper per kilowatt-day [4:262] while my system, calculated on an equivalent current density, will produce 31.6 pounds of copper per kilowatt-day. Thus, it is seen that this process can produce better results than ordinary electrowinning operations.

In concluding this section pertaining to laboratory work and results, I have attempted to discuss those problems which will be met in actual practice, not merely the theory of electrowinning. Numerous volumes have been written on this subject -- I applied the theory in my laboratory work, but this theory is only incidental to the aim of this thesis.

## III. PHYSICAL DEVELOPMENT OF A PLANT

In contemplating a change-over to the proposed electrowinning operation, no changes are necessary in any steps up to the converting process. Some changes may be helpful in the converting step, but no changes in structure will be required. It will be necessary, however, to design and construct a roasting furnace, a leaching system, and a tank room for electrowinning.

### A. The Converting Step

In converting matte to blister copper, some changes in converter operation may or may not be helpful. It is possible that an overblow in the converter, to produce $Cu_2O$, might reduce the amount of blowing necessary to produce $Cu_2O$ in the roasting furnace. Only an actual trial in the plant could determine the feasibility of an overblow. It must be noted, however, that too great an overblow might cause undue converter refractory wear due to the extremely corrosive nature of $Cu_2O$. Consequently, any advantages or disadvantages of overblowing must necessarily be ascertained by operations on a large scale.

### B. The Roasting Step

The design, construction, and operation of the roasting furnace is a matter subject to much arbitration and discussion. I believe that a furnace of the following specifications would prove satisfactory:

1. Inside furnace dimensions of 60 feet in length and 10 to 15 feet in width would give sufficient

capacity and provide enough area for oxidation while, at the same time, contain the air blast enough so that good oxygen-copper contact is provided.

2. Heat would be provided by means of gas burners located at one end of the furnace. The flame must be such that good oxidizing conditions are obtained in at least the rear two-thirds of the furnace. A temperature of at least 1250°C should be maintained in order that the $Cu_2O$ obtained would be liquid (the melting point of $Cu_2O$ is 1235°C).

3. A bank of tuyeres should be located directly below the gas burners. The tuyeres should project the air blast over the molten bath, not through it. In practice, tuyeres located in the side walls and projecting an air stream diagonally toward the rear end of the furnace might prove beneficial.

4. Waste heat boilers installed at the flue exit at the rear of the furnace will recover much of the energy lost in fuel consumption. If tuyere air is preheated by utilizing waste heat energy, a fuel saving will undoubtedly be realized.

5. The molten blister copper should be charged through a launder at the front or burner end of the furnace. A cover should be provided for the charge hole in order to prevent heat loss.

6. The $Cu_2O$ port, similar to a reverberatory slag port, should be located at the rear of the furnace, but in the side wall in order to escape the full blast of the burner flames. As the liquid $Cu_2O$ leaves the furnace, it should discharge to a running water launder. This launder will serve to granulate the $Cu_2O$, thus making possible faster leaching, and to convey the oxide to the leaching tanks.

7. The furnace should be built throughout of brick that is abrasion resistant and impervious to oxidizing conditions. Alumina, chromite, or carborundum bricks would provide these qualities. Insulation with high-temperature insulating brick would provide a considerable saving in fuel costs.

Since $Cu_2O$ is soluble in molten copper, turbulence of the bath must be prevented. The lighter weight of the $Cu_2O$ should allow the formation of a layer of $Cu_2O$ on top of the copper bath if mixing is prohibited. This top layer can be tapped off through the slag port in much the same manner as reverberatory slag is tapped.

Silver and gold will not oxidize appreciably at furnace temperatures and, consequently, as $Cu_2O$ is removed from the furnace, a build-up of gold and silver values will be realized. Therefore, it will be necessary to periodically (every month or so) tap the furnace of all the metal and recover the precious metal values by electrorefining methods.

C. The Leaching Step

Before the $Cu_2O$ is fed to the leaching tanks, the water which transports the oxide from the roasting furnaces must be removed. Perhaps the most economical method of removing this water is to discharge the launder flow on a sloping surface and allow natural drainage to occur. The water could be recovered by channelling the drainage to a common stream. The remaining oxide can then be transported to the leaching tanks by belt conveyor or any other suitable means.

The leaching tanks should be large cylindrical containers in which agitator arms rotate. At the bottom of the tank, inraking arms should rotate fast enough to move the copper that is produced during dissolution of $Cu_2O$, but slow enough so that the larger $Cu_2O$ lumps are not moved. Of course, the oxide must be fed at the rim of the tank. The solution agent (spent electrolyte) should be fed to the tanks at the bottom. This will provide better contact with the $Cu_2O$ also at the bottom.

The pregnant solution should be withdrawn by overflow at the top of the tank and go directly to the electrowinning section. The copper liberated during solution should be removed as a sludge at the center of the tank and recirculated to either the converters or the roasting furnace.

As shown in my experiments, rigid control of solution concentration is not necessary. However, control of concentration can be achieved by a controlled rate of $Cu_2O$ addition, a controlled rate of spent electrolyte addition, and a controlled agitaion.

D. The Electrowinning Step

The electrowinning plant construction and operation will be the same as many plants now in operation. Therefore, in view of the many excellent articles on this phase, it will suffice to say that the anodes should be cleaned every 12 hours, and that current densities may vary between 6 and 18 amperes per square foot without efficiency loss.

## IV. COMPARISON OF ELECTROWINNING AND ELECTROREFINING COSTS

As previously calculated, an electrowinning operation will produce 31.6 pounds of copper per kilowatt-day, while electrorefining with the multiple system will produce 165-180 pounds of copper per kilowatt-day. In order to produce 18,000,000 pounds of copper per month, an electrowinning plant will consume 25,160 horsepower-years of power per year. At a cost of $25 per horsepower-year (a figure suggested to me by Dr. J. George Grunenfelder), the power cost per year would be $628,000.

Taking 172.5 pounds as the mean value of copper produced per kilowatt-day in the multiple electrorefining process, power consumption per year will be 4,600 horsepower-years to produce 18,000,000 pounds of copper per month. This power will cost $115,000 per year, to which value is added $132,000 in interest loss. Thus, the total cost of electrorefining power consumption and interest loss is $247,000.

Comparison of both methods, other values being equal, shows that electrowinning would cost $381,000 per year more than electrorefining, costs having been calculated on the same annual production. It is probable that cost differences might be even greater because, although an electrowinning process would eliminate the fire refining furnaces and the casting wheel, this method would entail the construction of a roasting furnace and leaching tanks, as well as the cost of lead anodes.

## V. CONCLUSION

In view of the preceding cost figures, it is evident that copper production by the roasting, leaching, and electrowinning of blister copper cannot economically compete with copper production by the electrorefining process. However, if the cost of electrical power could be reduced to $6.44 per horsepower-year (calculated by the equation 4,600X + 132,000 = 25,160X), the electrowinning process could compete with an electrorefining system. Until such time, therefore, the interest lost on anode scrap and anode tie-up must be considered an unavoidable expense.

Future investigators might develop the feasibility of roasting copper matte and following through with the same operations as specified in this thesis. By controlling the sulfur content in the roast, a higher grade of matte may be obtained, a factor which would reduce the amount of material to be roasted and decrease the impurity content of the leach solution. This process, coupled with the elimination of the converting step, might prove economically practicable. I sincerely hope that, if any investigations are made along this line, this paper will be of some value.

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